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BROMEC8

Editorial

I hope you all had a relaxing summer (or be it a 'cosy' winter in the Southern Hemisphere). I hope you are ready to continue with more active and collaborative metals research. Some international and national meetings on metal conservation are planned for this year. One of these has already taken place in Brussels (see below). We will try to inform you about the forthcoming meetings/conferences when information becomes available. Dissertation topics for the 2003-2004 European university year are usually given in Sept-Nov. You will find some of these in this issue. Elsewhere, we continue our discovery through projects funded by the EU (see the EFESTUS project). Also, in this issue, you will find abstracts related to solders on precious metals and conservation problems on silver, copper and iron based artefacts. Two abstracts have been sent by Russian colleagues. It is a start and we hope that more contributions will come in the near future. We are still concerned about the lack of contribution from both Africa and Asia. Any suggestions to involve active people in these countries are more than welcome.

All BROMEC issues are now available on the ICOM-CC website (www.icom-cc.org). For those who do not know our research bulletin well it is a good occasion to go through the 8 issues and perhaps find a subject you are particularly interested in. To help you in your research you can use the new listing of abstracts by subject topics.

From now on, the national correspondents will inform you when a new BROMEC issue is available on the ICOM-CC website. Apart from that change, their role will remain the same. One important task for them is to collect the abstracts that are finally sent to me. Normally all abstracts should pass through the national correspondents for a preliminary reading. It would be very good if everyone would respect this obligation so I can then discuss your abstract with another neutral person.

Brussels international conference: *Metals, conservation and research* held on 24-25 October was an occasion to promote our work within the Metal Group. To find the programme of the conference, visit the website of The Asociación de Restauradores sin Fronteras that organised the seminar (www.restauradores-sinfronteras.org). Proceedings should be published in the near future and we will inform you as soon as they are available. In November, another Metal conference is scheduled for Porto (see general information section) and I will take the opportunity of this other meeting to present our work to our Portuguese colleagues.

This issue of BROMEC has been copy-checked by James Crawford, Australian objects conservator working at IRRAP, France. As an 'antipode' and a native English speaker, he will bring another perspective to BROMEC. He aims to facilitate communication of the readership by improving the English of the translated texts. This should reduce ambiguity and generally aid the flow of the text for readers. This objective will prove most useful for those group members who are reading English as a foreign language. His work will involve rearranging convoluted and confusing sentence structures. This will therefore simplify the phraseology - making BROMEC more accessible for all. This work will continue on forthcoming issues and aims to evolve in a manner that leads to maximising the communication potential of the truly international and important forum that is BROMEC. Before submission to your national correspondent, please continue to thoroughly proof-read abstracts, especially those that have been translated into English. We always welcome suggestions on improving the clarity of communication in BROMEC. As a metals conservator he is also assisting me with the scientific editing. James has kindly offered this initiative which is greatly appreciated.

The editor
Christian DEGRIGNY
The assistant editor
James Crawford

Contents

Ongoing research projects

EFESTUS: Tailored strategies for the conservation and restoration of archaeological valuable Cu-based artefacts from Mediterranean Countries (***CNR-ISMN***)

The general objective of the European EFESTUS project is to identify the degradation causes of well-defined groups of Cu-based archaeological valuable artefacts selected as a function of their archaeological context and of their chemical composition and structure.

Starting from this basis, innovative or traditional methods, stemming from local participation, will be used for the restoration and conservation of the archaeological artefacts. This will be done after validation tests have been carried out on Cu-based reference alloys with a microchemical structure similar to that of the ancient alloys.

The project intends to develop, validate and disseminate tailored approaches for slowing/retarding the degradation phenomena of archaeological valuable bronze artefacts and for preventing further damage in museum showcases and storage areas.

The five specific scientific and technological objectives of the EFESTUS project are briefly reported as follows :

- selection of archaeological contexts and bronze artefacts representative of different possible deterioration phenomena and identification of the chemical and physical degradation mechanism. The archaeological objects could be coins, weapons and small or large artistic objects ascribed to the following material classes : Cu-Sn, Cu-Zn, Cu-Pb, Cu-Sn-Pb and Cu-Zn-Pb;
- production of Cu-based reference alloys characterised by a microchemical structure similar to that of the ancient alloys and whose chemical composition is ascribed to the following material classes : Cu-Sn, Cu-Zn, Cu-Pb, Cu-Sn-Pb and Cu-Zn-Pb;
- design and production of tailored conservation materials to be used for each specific degradation phenomenon;
- selection of the appropriate material according to the restoration and conservation procedures;
- development of an integrated information system allowing communication, control and exchange of information within the partners and European and Mediterranean Museum and Conservation Institutions; and
- production of an atlas with detailed physical-chemical information on the selected Cu-based artefacts related to the burial conditions, degradation mechanisms and conservation methods.

The partner institutions for this project are from Italy, Spain, Greece, Turkey, Jordan, Tunisia, Algeria and Egypt.

Contact: Gabriel Maria Ingo (coordinator - CNR-ISMN).
Funding: INCO-MED programme. European Commission

Ongoing research projects

Investigation and restoration of iron sheets and decorative stars on the doors from the pilgrimage Church of St. John of Nepomuk at Zelená Hora - Green Mountain (***NIPM***)

The premises of the pilgrimage Church of St. John of Nepomuk, built by J.B.Santini, at Green Mountain near Žďár on the Sázava River, has been a national cultural monument since 1995. Around the perimeter of the baroque Church are five double-doors and four single-doors built within stone frames. After preliminary investigation all the doors were reconstructed and restored in the vein of the original building to preserve the ideology, material and shape. The objective of the project was to provide long-term protection and at the same time to respect the authenticity of the original surface treatment. Mutual communication between the specialists involved was a prerequisite.

The sheet metal covering was badly corroded (in some places mineralised on the whole thickness) and the original surface finish was 90 % degraded and covered with corrosion products. Holes had been drilled on the wrought iron sheets which have ground edges. The decorative stars, which are also heavily corroded, are made of thicker sheets than the sheet covering the doors. Remains of silver-like metal are visible on the large-size stars. Similar remains of yellow metal can be observed on the medium-size stars.

The investigation included specifying the original colours on the doors' metal sheets and the surface treatment applied (tinning, silvering, gilding) to the decorative stars. When searching for the coloured layers of the sheets, it was assumed that the doors were originally black or green. Analysis of samples from the surface showed that the innermost white layer was a basic paint containing white lead, the next layer was green containing the classical greenish blue pigment - malachite. A cross section of a door sheet confirmed that within the stratigraphy the black layers appear closer to the surface and have consequently been applied more recently. After careful blasting of the metal sheets, a thin black coat adjacent to their surface was observed. Microscopic examination and XRD of samples from the layer revealed the presence of magnetite (Fe_3O_4) and wüstite (FeO). It is supposed, that these compounds were formed during the forging process and are then part of the original surface. Further analyses were carried out using XRF and SEM/EDS. The presence of lead was confirmed in cross-sections of the protective layer, but small amounts of tin was also found (89 % Pb and 9 % Sn). Silver was detected on cross sections of samples from the large and small-sized stars. Presence of gold on the medium-sized stars was revealed directly from a powder sample.

After consulting conservators it was agreed that from the total 60 pieces of the original preserved door sheets, 10 selected pieces from just 3 of the double doors would be restored. The other sheets would be stored on the premises and would be kept in optimum conditions in an enclosed space to slow down their further degradation. To preserve the original protective layers, wax was applied. The type of replacement metal sheet was selected for its metalworking properties so that it could be modified and inconspicuously incorporated. These new sheets were repeatedly tilt-hammered and their surface was deformed in such a way to visually imitate the heavily corroded sheets. This relatively massive substitution of the original sheets was carried out in view of the poor state of the original material and the high physical load when installed in the original place. The synthetic paint system was selected for its long durability and favourable aesthetic appeal. The paint was applied on a surface prepared by careful blasting and passivation with tannate solution. The surface of the stars were blasted, missing mandrels reconstructed and the short ones completed. The large and the small stars were tinned (in the ratio of 60 % tin to 40 % lead), remains of the original tin on the inner side of the stars were not completely removed. The medium size stars were gilded with gold leaf on a basic paint system identical to the paint system used for the sheets.

Contact: Alena Havlínová (NIPM)
Funding:?

Ongoing research projects

Reduction of silver tarnishing and protection against further corrosion (***UPR 15 / CNRS***)

Due to their tarnishing, silver objects are removed from exhibition in museums as cultural heritage artefacts. To avoid this, they are regularly polished and protected with a transparent film. However, the mechanical cleaning consumes the silver material and the protective film often modifies their appearance. These conservation practises are therefore not satisfactory. Artefacts may be put into a hermetic display-case, sometimes in presence of gas-phase inhibitor, but this cannot be applied in all situations.

We are proposing new methods to confront the problem. Experiments were carried out in four steps: 1. Formation of the initial tarnish, 2. Cathodic reduction of the tarnish layer, 3. Surface treatment to reduce further corrosion, and 4. Exposure to accelerated corrosion tests to assess the effectiveness of the protection [1].

The tarnish (50 to 100nm) was formed on polished pure silver surface immersed 1 hour in 10^{-2} mol/L Na_2S solution. It was reduced in sesquicarbonate solution at a constant potential or a constant current. Once the tarnish was reduced, two protection systems were tested: a self-assembling membrane (SAM) of thiol [2] already known in the electronic industry and an electropolymerized film of amino-triazole [3]. The thickness of the latter is a few tens of nanometres. Both films are completely transparent and do not modify the visual aspect of silver artefacts.

The kinetics of tarnish formation during the initial step, the reduction of tarnish film, and final step were monitored by open-circuit potential, electrochemical quartz crystal microbalance, and reflectance measurements.

It was found that after the tarnishing process, the reflectance of the silver surface decreased from 100 to 25% and that the electrochemical reduction of tarnish layer returns the reflectance close to 100%. A good protective performance was achieved with the thiol SAM layer. Results showed only a few per cent loss of the reflectance when subjected to the accelerated corrosion tests. However, it was found that the electropolymerized film of amino-triazole has no protective effect.

The thiol SAM layer is reversible since it can be dissolved in pure isopropanol.

1. Trachli B.,Keddam M., Srhiri A. & Takenouti H., Corrosion Science., 44 (2002) 998
2. Evesque M., Keddam M. & Takenouti H., 8th International Symposium on Electrochemical Methods in Corrosion Research, May 2003, Nieupoort (elgium)
3.Keddam M., Klein L., Takenouti H. & Trachli B., 15th International Corrosion Congress, paper n0 701, October 2002, Granada (Spain)

Contacts: M.C. Bernard, E. Dauvergne, M. Evesque, Michel Keddam, and Hisasi Takenouti (UPR 15 / CNRS***)***
Funding: CNRS funds. This work is performed in the framework of the GdR "CHiMart

New research project

Restoration of cultural heritage: stainless steel as an alternative (***LRMH***)

Although they are not visible, almost any historical monument contains several parts made of ferrous alloy (cast iron or steel), originally chosen to give mechanical stability and sustain the construction. These have been playing their role for a long period of time. Nevertheless, after decades or even centuries of exposure to all weather conditions, they are often in quite a poor state of conservation. In many cases it is not only the metal which is seriously damaged. In turn, the metal's corrosion products, owing to their greater volume and higher oxidant power, are very harmful to the other material components of the monument.

In very specific cases, to prevent further degradation or for safety reasons, the original corroded material has to be partially or completely replaced, although this procedure should contradict some ethical conservation principles. The most common are: metallic sculptures (in bronze, lead or any other alloy, where forged iron is usually used as internal reinforcement); stone sculptures (where gudgeons are very frequent) and stained glass (where the use of a saddle bar is necessary to maintain the glass in the window casing). Stainless steel is used as an almost systematic substitute in these cases, and although its properties are very well known, the application of the commercial types of alloys to the very specific needs of the restoration of historical monuments is far from being well exploited. To study these problems a research program was initiated at the "Cercle des Partenaires du Patrimoine". The principal goal of the programme is to propose technical cards to drive the users towards a correct choice (type, assembly and finish).

A survey was recently performed with restorers about details of choice, assembly and finish of stainless steel as a substitution material for the restoration of historical monuments. Aiming to cover a broad field of possibilities, experiments were also run with other materials commonly used by restorers, such as: pure iron, carbon steel, brass and also iron-nickel alloys, recommended in the case where a low coefficient of thermal expansion is required. In order to evaluate their performance, these materials were tested in three different conditions:

- Individually and in contact with copper, zinc and lead:
    - exposure for more than three years on the top of Saint Denis Cathedral (suburbs of Paris, France) where an atmospheric corrosion site already exists;
    - exposure for one year in a humidity chamber;
    - electrochemical measurements: passive-active behaviour and galvanic couple
- In contact with fixing products (mortars, resins, etc) commonly used by restorers
    - exposure in a warm and humid atmosphere;
    - electrochemical measurements, performed in an aqueous extraction of the fixing products
- In contact with stone and fixing products
    - exposure for several years on the top of Langres Cathedral (France) (known for remarkable climatic variations);
    - exposure for 8 months in a climatic chamber (cycles from -10 to +60°C)

Results evidenced the good performance of stainless steel in the conditions described above. Their general resistance to corrosion was better than that for all the other tested alloys. Nevertheless, because this resistance is mainly due to the "barrier characteristics" of a passive layer, caution must be taken when working and assembling the parts, particularly in the case of welding, surface contamination and damage.

Contacts: Virginia Costa & Annick Texier (LRMH)
Funding: Cercle des Partenaires du Patrimoine / USINOR

Ongoing research projects

Research into the possibilities for the removal of tin solders on silver artefacts (***ICN, RM***)

This final thesis project was presented in BROMEC 5 and it aimed to find answers to the following questions:

- What are the microstructural changes in silver when treated with tin solder?
- How deep does the tin or lead diffuse into the silver (and vice versa) and at which temperature?
- Can old tin solders be removed?
- Which tin solder removal treatment causes the least damage to the silver matrix?

From the late Middle Ages onwards, soft soldering on silver during manufacture was limited. In fact, soldering has mainly been used for repair, by either conservators, gold and silversmiths or non-professionals. The damage induced by solder to silver is evidenced by a surface that appears to be dissolved or eaten away. Research was performed to determine the causes of this phenomenon.

Reproductions of solder on silver showed limited interaction between solder (50Sn-50Pb) and sterling silver. The interaction was found to be, diffusion, intermetallic compound (IMC-Ag_3Sn) formation and dissolution of silver into the solder. The formed Ag_3Sn layer slows the dissolution of silver into the solder. However, above a temperature of 480°C, the Ag_3Sn is no longer stable and the silver can be dissolved by the solder at a higher rate. Upon cooling, alloys (solid solutions) made from the object and repair material are formed.

So the problem of the solder/silver corrosion phenomenon is due to interaction between the solder (or IMC) and silver, at temperatures above 480°C. The interactions are based on diffusion and penetration, followed by dissolution and the formation of new alloys. Some preliminary tests were also conducted to study the removal of solder from silver with chemical methods. Further research is required to draw final conclusions.

Contacts: Maickel van Bellegem, Bart Ankersmit (ICN) & Robert van Langh (Rijksmuseum)
Funding: ICN

Ongoing research projects

The *Nottingham Galley* cannon collection: A proposed scientific inquiry into the reasons a conserved iron cannon dramatically cracked into pieces whilst in storage (***HTACL, DCUoM & DMCUoM***)

The English merchant vessel *Nottingham Galley* was lost when it struck Boon Island off the Maine (USA) coast in December of 1710 [1]. The ship's company was stranded for 24 days in abysmal conditions and resorted to cannibalism before rescue. In 1995, nine iron cannons and one cannon fragment from this wreck were recovered by the State of Maine to prevent salvagers from stealing them.

The cannons were conserved using electrolytic reduction in alkaline (sodium sesquicarbonate followed by sodium hydroxide) solutions for 3 years. Chloride extraction was monitored all throughout the process. The cannons were waxed and returned to the Maine State Museum in 1999 where they went into off-site temporary storage. This storage area was heated in winter and could get very hot in summer, 93°F- 33.9°C, with high humidity, 88%RH, with a possible change of 24% RH in 24 hrs.

After three years in storage, one of the cannon dramatically cracked into pieces and three other cannons showed signs of instability. A lot of fine, crumbly corrosion products poured out of the cracked cannon and a quick silver nitrate test showed a strong positive response. Dried droplets, evidence of weeping iron, could be observed at the surface of the cannon. We believe the cannons may have incomplete chloride removal and were aggravated by a poor storage environment, resulting in at least one cannon suffering catastrophic destruction. To confirm this assumption a scientific inquiry and testing scheme was proposed by the authors.

The first task was to review the original treatment records to discover the treatment each cannon experienced. We discovered that more than one cannon were treated per tank. The chloride data (mercuric nitrate titration) reflects the concentration of chlorides for two or more cannons and does not represent the extraction rate for a particular cannon. Furthermore, there was a doubt concerning the level of electrical contact on the cannon that cracked apart. When trying to drill this cannon to attach the electrical connections no solid metal could be hit at the muzzle end. It may have been then more corroded than the others. There are no records of the specific electrolytic reduction performed on the cannons.

After cathodic reduction the cannons were rinsed/soaked in tap water for a few days, and soaked in a tannic acid solution for a few hours. They were then immersed in unmelted wax (probably microcrystalline) and both the wax and cannons were heated up at the same time until the cannons sank into the warm wax. For days, the wax was very hot and the cannons evolved bubbles and steam. Then the wax cooled, solidifying with the cannon inside. The wax was then sufficiently rewarmed to remove the cannons. This was to avoid the hot wax pouring off a very hot cannon. Not all the excess wax was removed, on the premise that a bore full of wax was thought to impart good physical support.

Our second task was a literature search of cannon treatments. This confirmed, that at the time of this project, electrolytic reduction was a good choice of treatment for the iron cannons if carefully controlled. We found that the amount of extracted chloride ion in solution may not accurately reflect the concentration of residual chloride ion in the artefact. There is little published data on the experimentally determined "safe" level of residual chloride ions for archaeological iron. This level may ultimately be linked to the environmental conditions archaeological iron is exhibited or stored at.

Our last task is in progress and it aims to characterize each cannon's condition. We propose to drill the destroyed cannon first and assess the residual chloride ion content by digestion of the sample. We also propose to evaluate the type of cast iron present and identify the corrosion products.

It is hoped that the comparison of the residual chloride ion level with other cannons (that are thought to be stable), might be able to indicate a level of residual chloride iron that might represent a potentially unstable threshold. Barring this, perhaps we will be one step closer to being able to evaluate if retreatment of a dried cannon (with "X" amount of residual chloride ion content) can be successful in reducing the level of chloride contaminant. Ultimately, we will need to test the remainder of the cannons and evaluate retreatment for the entire collection or design exhibit/storage parameters for the collection to keep them as stable as possible.

1. Warner, R., Part 1, "The Wreck of the *Nottingham Galley*", in Boon Island, by Kenneth Roberts. University Press of New England, 1996, pp. 3-21.
2. Carlson M.O. Bruce M.R.M. & Riess W.C., The *Nottingham Galley* cannon collection ca. 1710: A proposed scientific inquiry into the reasons a conserved iron cannon dramatically cracked into pieces in storage, in Preservation of Heritage Artifacts of the NACE Northern Area Eastern Conference, Corrosion Control for Enhanced Reliability and Safety, Ottawa, Ontario, Canada, September 15-17, 2003.

Contacts: Molly O'Guinness Carlson (HTACL), Dr. Mitchell R. M. Bruce (DCUoM) & Dr. Warren C. Riess (DMCUoM)
Funding: excavation and treatment were partly funded. As regards to the last task, the authors applied for a grant. The work presented in this abstract is on hold until that grant comes through.

Ongoing research projects

Study and conservation of a selection of copper cast artefacts (***VB/GACC***)

In 2002, the Vologda Branch-office of the Grabar Art Conservation Centre and Cyrillo-Belozersky museum's reserve began a joint project to study and conserve a selection of artefacts within the small copper cast collection owned by the museum's reserve.

The collection consists of 136 objects. These are icons, folding icons and their fragments and crucifixions crosses. All of these objects formed parts of the museum collection in various ways and at different times. Many of them have decorative covering such as gilding, silvering, enamel, etc. It is necessary to note that such objects bear no stamps/marks/hallmarks, which could contain the artisan's initials, place and date of their manufacture. Our collection is not an exception here. That is why, in the course of the object identification, the external typological (iconographic, stylistic, epigraphic) attributes are normally used.

In the framework of the joint project we wanted to study a selection of 20 objects and to combine artistic and historical researches with physical and chemical investigations to obtain more information about each object. Physical and chemical investigations are usually performed during the conservation work. For our collection, these investigations were conducted at the Laboratory CNT (Centre Of New Technologies) in Saint-Petersburg. Artistic and historical researches in archives were performed in parallel.

Qualitative and quantitative information on the materials such as their composition, the metal-work of the covering (silvering, gilding, etc.), the nature of the coloured enamel or other decorative finishing were obtained using SEM observation and Electron Probe MicroAnalysis (EPMA). In addition to the previously listed instruments, the following instruments were also used;

- Simultaneous semi-conductor spectrometer LINK AN-10000 for the analysis of basic elements; and
- Consecutive spectrometer MICROSPEC for the analysis of impurities and traces of elements.

The physical and chemical investigations allowed to determine the manufacture date of some objects more precisely and confirmed the art-historian's assumptions. Furthermore, it is now possible to classify some groups of objects, which have either a similar composition or similar decorative finishing.

The first results are promising. Similar comparative researches of the collection could certainly allow us to draw some generalizing conclusions.

Contact: Natasha Smirnova (VB/GACC)
Funding: Cyrillo-Belozersky museum reserve

Ongoing research projects

Examination of archaeological artefacts to assess the average corrosion rates and study the long term corrosion mechanisms of low carbon steel in soils (***CEA, ANDRA***)

In the context of the storage of French nuclear waste, a multi-barrier disposal system is envisaged. Wastes could be put in metallic overpacks deposited in a clay soil. As these overpacks could be made of low carbon steel, it is important to understand the corrosion behaviour of this material in soil during a period of several centuries. So, it is necessary to consolidate the empirical data by a phenomenological approach. This includes laboratory experiments and modelling of the phenomenon that have to be validated and completed by the study of archaeological artefacts. This was the aim of this PhD-work.

For this purpose, an analytical protocol was developed: about forty archaeological artefacts coming from five dated sites (2nd to 16th centuries AD) have been studied in cross-section to observe, on the same sample, all the constituents of the system: metallic substrate/corrosion products/environment. The corrosion products are divided into two zones: the Dense Product Layer (DPL) in contact with the metal, and the Transformed Medium (TM) which are the corrosion products formed around soil minerals (quartz grains etc).

The metallic substrate has been studied by the classical methods of materials science (optical and scanning electron microscope, energy and wavelength dispersive spectroscopies). It has been verified that despite their heterogeneity of structure and composition, they are all hypoeutectoïdes steels that can contain phosphorous up to 0.5 wt%. The corrosion products have been analysed by the local structural analytical methods of microdiffraction under synchrotron radiation (µXRD) and Raman microspectroscopy. These two complementary techniques and also the elemental composition analysis were conducted for the characterisation of the corrosion forms. In the majority of the samples coming from four sites, the DPL are constituted by goethite including granules of magnetite/maghemite. On the artefacts from the fifth site, a particular corrosion type has been identified. Present with other products of corrosion, this particular corrosion type, a siderite layer is due to a particular environment: waterlogged soil containing wood. Overall, analyses conducted in the TM show that it is composed of poorly crystallised goethite when compared with those of the DPL. In addition, in the TM zone the average elemental iron amount decreases progressively from the level closest to the metal towards the soil (in which the concentration level stabilises).

In order to know the behaviour of the identified phases in wet soil, some thermodynamic data have been used to calculate their solubility in function of pH, potential and various water compositions.

The first drawn conclusion is that the influence of the composition and the structure of the material do not strongly affect the corrosion behaviour. From the results, some hypothesises have been formulated on the long term corrosion mechanisms of hypoeutectoïdes steels in the considered environment. The role of the cracks formed in the DPL during the burial was evidenced. Moreover, these corrosion products undertake a dissolution in the soil water and a reprecipitation, explaining the progressive decrease of the iron amount in the TM.

Lastly, some average corrosion rates have been measured with the help of the analytical and thermodynamic results : they do not exceed 4 µm/year.

Contact: Delphine Neff (CEA)
Supervision: Gérard Béranger (UTC) et Philippe Dillmann (CEA Saclay)
Funding: CEA & ANDRA

New research project

Laser Cleaning of Metal Surfaces (***ISC***)

Metal alloy monuments suffer tremendously from the impact of atmospheric pollutants, and therefore require regular maintenance and cleaning. A research project has been set up in Germany to systematically evaluate the interaction of laser energy with various metal surfaces. The project team consists of conservation scientists and laser experts from two Fraunhofer institutes, two restoration companies (for performing and controlling the transfer into practice), and a material research group directly connected to a state preservation department, ensuring curators' control on the cleaning measures. The project started in mid 2002 and will run for a total of three years.

The investigations focus on the ablation of surface deposits caused by outdoor or indoor weathering such as corrosion crusts, aged preservation coatings, dirt deposits, graffiti, traces of paint, lime or rust. The experiments are mainly dedicated to unsolved cleaning problems existing for copper and copper alloys (bronze, brass), iron, and gilded monuments. Tests have first been performed on cast model coupons after artificial ageing and on corroded substrates originating from cast-off originals. The results will be directly transferable to metal monuments with comparable surface phenomena.

Alteration and ablation thresholds, and alteration effects of underlying substrates worth preserving (e.g. patina of copper and bronze) have been determined by the systematic variation of relevant laser parameters. These include fluence (Energy of the beam/surface), integral pulse number, and repetition rate. Regarding laser sources, the available wavelength region from the UV to the near IR with special relevance to portable Nd:YAG-systems (λ = 1064 nm as basic wavelength, 2. and 3. harmonics) has been covered. Surface absorption measurements in the UV / VIS / IR wavelength region are completing the interaction studies.

Meanwhile, the cleaning capability of a portable Nd:YAG system (λ = 1064 nm) has been proven with applications on test objects in restoration workshops. With respect to the threshold results obtained on model samples, promising cleaning results could be stated for copper, brass, gilded objects, and partly for bronze. Especially for the latter, the quality of cleaning strongly depends on the objects' alloy compositions and surface properties. In all the successful cases (defined as where the surface deposits could be removed), the patina, bulk metal, or gilding was not affected.

At present, the comparison between laser treated surfaces and areas, cleaned with established techniques, is under investigation.

The current project results have recently been presented and published at LACONA V (Conference 'Lasers in the Conservation of Artworks'), held in September 2003 in Osnabrück, Germany.

Contacts: Peter Mottner (ISC)
Funding: Deutsche Bundesstiftung Umwelt (German Foundation for the Environment)

New research project

Metal objects in museums: experimentation and implementation of a conservation assessment and collections condition survey data file system on the armour collection of the "Palazzo Venezia" National Museum in Rome (***ICR***)

During the year 2001, the Ministry for Cultural Heritage has published the "Guidelines on technical-scientific criteria and on managing and developing standards in museums". These guidelines define the minimum quality standards that every Italian museum should adopt. According to these guidelines, each museum should be equipped with a data file system for Conservation Assessment and Collections Condition Survey.

As diploma work at the Istituto Centrale del Restauro (ICR) conservation training school, students Marta Giommi and Sara Sgarzi are practically testing such a data file system (already created) in some storerooms of a national museum with historical collections (Odescalchi's weapons and armour collection). Through this experimental work, implementation of the data file system should be accomplished in order to develop a valuable tool for programming and managing conservation strategies in museums.

Since this data file system is organised in two levels of records (the second being an elaboration of the first), the Collections Condition Survey incorporates, at the first level, a survey based on a statistical methodology and the use of a common record for all types of collections. At the second level, different models for the survey of each different type of object in the collection should be developed.

For this second level of documentation, a model for metal objects will be tested (this model is intended to work also for metal composite objects). It should contain all the information required for a comprehensive knowledge of the object and its conservation condition (conservation history, materials, techniques, conservation condition, required conservation treatments and storage/display/usage conditions).

To fill the record a pre-defined technical lexicon will be provided in order to ensure a homogeneous data gathering that will consequently enable having the possibility to properly compare data. Since a common standard lexicon for metal objects techniques and conservation condition description is still lacking, an illustrated glossary will be carried out to further support the record compilation.

We are aware of the wide scope of this work and its complexity, but we hope that it will become a valuable starting point for further studies. To achieve this goal, the objective is to formulate a standard conservation data file system for Italian museums and a standard metals conservation technical terminology, which could be used in an unambiguous way by any professional.

Contact: Bianca Fossà (ICR)
Students: Marta Giommi, Sara Sgarzi
Funding: no external funding

New research project

Restoration and conservation of damascened steel weapons. A case study (***ICR***)

The thesis work by Fabiana Cangià at the Istituto Centrale del Restauro (ICR) aims at enlightening and defining some aspects related to the conservation of damascened steel weapons. The first issue is the definition of *damascened steel:* meaning, history, technology, physical-chemical characterisation, degradation processes and effects on a material which is as famous as little known.

The study will then include a bibliographic survey on conservation treatments that have been carried out on such a wide category of objects, considering the different typologies and materials. In order to evaluate ethical and chemical/physical efficiency, it will then thoroughly review the most popularly performed treatments.

Based on that knowledge, we will treat an 18th century Indo-Muslim sabre, from the "Armeria Reale" (Royal Armoury) in Turin. This sabre represents quite an interesting case study, not only for its precious damascened steel blade from India, but for the presence of several other materials (gold, silver gilt, jade, textile, leather, wood), which will require different conservation treatments.

Contact: Stefano Ferrari (ICR)
Student: Fabiana Cangià
Funding: no external fundings

New research project

<u>The problems associated to the past use of soft solder in the repair and restoration of golden objects</u> (*HA/**RAFA***)

Solder on golden objects is normally made of hard gold solder. Due to occasional damage, for example, physical/mechanical breakage of delicate parts, these objects were often repaired with soft solders made of lead/tin alloys that flow easily because of their low melting point. In some cases, these soft solders also have additional alloying elements such as bismuth or cadmium. But these solders cause damage by diffusing into the precious metal. Furthermore, because soft solders are not as strong as hard solders (with high melting point) they have to be redone relatively more regularly causing even more damage.

It is not known exactly how much the solder can damage the gold alloy by diffusion and which metal(s) in the solder initiates the problem. To re-solder a golden object with soft solder is not considered as an "ethical conservation treatment". The joint itself may be quite reversible by heating the object, but the diffusion of the solder into the original base metal is irreversible and the soft solder diffuses deeper each time the object is heated.

The purpose of this thesis is first to list all possible damage that can be caused by the alloying elements of the soft solder. Based on these results, we will study alternatives to the use of soft solder and also protocols to remove and replace inappropriate soldering.

The thesis will include;

- A review of the history and composition of soft solders used in the past on gold artefacts (studying recipes of solder alloys and fluxes);
- An examination of the damage caused to the gold by use of soft solders and more particularly the way they diffuse into the metal. For this purpose, a number of samples will be prepared. The first series will be used to examine the diffusion of different soft soldering alloys into a layer of 18 carat yellow gold, combined with different temperatures and different durations;
- A review of the different methods to remove previously and currently employed soft solders and of the best techniques conservators can use to resolve the problem. This can be done mechanically, chemically or galvanically. The results will be evaluated through the resultant damage and the effectiveness of the removal, as carried out on a second series of samples; and
- Alternative reassembly treatments. Preliminary tests with high-strength adhesives, such as epoxies, are promising.

To realise this thesis, normal light microscopy, SEM-EDS investigation as well as Micro-XRF will be performed at the University of Antwerp (UoA), Chemistry Department. The thesis will be promoted by Patrick Storme and co-promoted by Thessa Goossens (Hogeschool Antwerpen). This subject was originally a project of Dr. Jack Ogden from Hildesheim, and has gratefully been received as a thesis subject. Dr. Jack Ogden will also act as supervisor.

Old references of recipes to remove soft solders from objects are still welcome to complete the review of literature on this subject.

Contact: Dietlinde Peeters (student, Department of Conservation-restoration, HA/RAFA)
Funding: no external funding

New research project

<u>Research on the bonding of metal structures to stone bases, i.e. for metallic sculptures</u> (***HA/RAFA***)

When metallic sculptures are restored, often armatures and reinforcement in the bases are in poor condition. There is not a lot of information on efficient techniques and materials when restoration or replacement is needed.

The aim of this thesis is to find out which fixing products were used to embed metallic rods into the base of stone, both in the past and present. Examples of these embedding materials are: mortars, lead, sulphur, resins.

Special attention will be drawn to the use of sulphur, which is not well documented yet, and also to the use of alloys that expand while cooling down.

The different materials will be tested as regards to their physical properties as well as their compatibility with both the stone of the base and the stainless steel reinforcements. Physical properties will be tested by using the pull-out test (to measure the strength of a material, an adhesive or a casting-in, by means of a mechanical drawing-bench) and artificial mechanical ageing. To indicate the compatibility of the materials with the stainless steel, electrolytic tests will be performed by drawing polarisation curves.

Through such testing, an indication of suitable materials and techniques that minimise the adverse affects of fixing systems in stone bases will be researched.

This project will involve different partners within the Hogeschool Antwerpen: the department of Conservation-restoration (Patrick Storme, head of the metal restoration section) and the department of Industrial Engineering (Ing. Dirk Anthierens).

Any experience on methods of fixing sculptures into bases, materials used for that purpose or any other information or contacts related to this subject would be received with much gratitude.

Contact: Elke Otten (student, Department of conservation-restoration, HA/RAFA)
Funding: no external funding

New research project

Development of a diagnostic method and a phenomenological scenario for the alteration of cultural iron materials exposed to atmospheric corrosion (***LRC CEA/ CEA/CNRS – LRMH/C2RMF***)

Atmospheric corrosion of iron used in cultural heritage buildings, statues and other artefacts is a problem of great importance. Particularly, the evaluation of the corrosion rate i.e. whether the iron is relatively passivated or not by the layer of corrosion products that forms on it. This evaluation is linked to the eventual restoration decision. The reliable diagnosis of atmospheric corrosion behaviour of an iron artefact could indeed allow both to save money when restoration is not necessary and to decide to perform works when the metallic structure is under threat. A 2 year-project entitled "Understanding corrosion mechanisms and assisting the evaluation of the corrosion rates and behaviour prediction" , has been submitted to the French Minister of Culture which has agreed to fund it.

The project will be conducted in partnership between the following governmental institutions and laboratories; LPS CEA/CNRS; IRAMAT CNRS; LRMH; C2RMF; LADIR CNRS; and ICMCB is formulated in two parts. The first part deals with the understanding of the wet/dry cycle that initiates the atmospheric corrosion of iron and is linked to the nature of the electrolyte film that condenses on the iron surface. This mechanism, proposed by Evans and Strattmann assumes that, in the first stage of the cycle, the corrosion products themselves play a role in iron corrosion. This important point, and others, need to be checked experimentally before proposing a modelling of the corrosion cycle. The second main aim of the study concerns the corrosion rate evaluation. Because the corrosion products, particularly the two main phases : α -FeOOH goethite, and γ-FeOOH lepidocrocite, are involved in the corrosion mechanisms, the ratio of these two phases could reflect the reactivity of the corrosion scale i.e. the corrosion rate.

Well dated historical samples, will be studied in order to determine the α/γ ratio evolution and to link it with the electrochemical behaviour of the rust. In addition, reference ferrous alloys will be exposed to several atmospheres at given sites where atmospheric parameters are measured and will be studied.

Last, but not least, it is well known that some elements coming from the environment (chlorine, sulphur), but also present in low quantities in the materials (copper, phosphorus), can influence the atmospheric corrosion of iron. This influence will be studied in a second stage.

Contacts: Philippe Dillmann (LRC CEA/ CEA/CNRS) & François Mirambet (LRMH/C2RMF)
Funding : Programme national de recherche sur la connaissance et la conservation des matériaux du Patrimoine Culturel. Ministry of Culture funding.

Calls for collaboration

Thermal treatment of archaeological iron (***DC/OCM – DSC***)

This final thesis conducted at the School of Conservation in Copenhagen aims to study the thermal treatment of archaeological iron (in daily language: "Annealing"). In brief, this process consists of treating archaeological iron by heating it in a furnace, primarily to remove chlorides.

The method in Denmark dates to 1858, where Mauritz Rasmussen Schmidt began to experiment with annealing as treatment for marine iron at the Danish Defence Museum (Tøjhusmuseet). From 1867, Steffensen and Rosenberg continued this work at the National Museum, although with some modifications. The method is still used today, although alternative conservation methods for unstable iron are being examined and used in Denmark (see Bromec 1, Lars Andersen et. al).

The "Standard Procedure" is to heat the furnace with the items at a slow rate to approximately 800°C and maintain that temperature for about 20 hours or more. The atmosphere is either neutral (Nitrogen) or reducing (Nitrogen/Hydrogen mixture or pure Hydrogen). The purpose is to bring the chlorides to a gaseous state, to be able to remove them quickly. After treatment, the artefacts are usually impregnated with wax. Actively corroding excavated iron can thereby be stabilised.

The method has been criticised to be destructive and to alter the structure of the iron, thus destructing metallurgical information that is so important to understand the manufacturing techniques. Although samples for technological investigation can be taken out before treatment and specific items left untreated and dry stored, the method itself still needs further development.

This work aims to clarify the advantages and disadvantages of the method, with focus on minimizing the disadvantages by experimenting with the different parameters (temperature, pressure, heating duration etc.) and recording the success rate (chloride removal) and the effect on the metallurgical structures of the iron. Furthermore, a monitoring method for the ongoing process is under development.

A questionnaire follows this abstract to perform a survey on stabilisation treatments used on archaeological iron. We are particularly interested in whether your department use or have used heat treatment for archaeological iron or consider doing so. Considerations that have led to the discarding of the method are also very welcome.

Please write your answers by referring to the question numbers and send them to the address indicated by ordinary mail or e-mail: jaa@odmus.dk. Also please remember to write your contact information: Institution, name, address etc.

Contact: Jens Gregers Aagaard (DC/OCM)
Funding: no external funding

Questionnaire

Do you use the Annealing method for Archaeological Iron?

If yes

1. Do you have a furnace of your own?
2. If no, where is your annealing performed?
3. Do you have criteria(s) for the type of objects you anneal?
4. Do you have criteria(s) for the execution of the annealing?
5. How is the iron treated before annealing?
6. Could you give a description of your annealing process?

    including
    a. Annealing atmosphere
    b. Timing in the heating process
    c. Heating time at maximum temperature
    d. Temperature curve versus time
    e. If obtained: Measurements and monitoring of the annealing process

    Please feel free to write about the considerations behind the chosen parameters.

7. How is the iron treated after annealing?
8. What is your assessment of the method and additional experience with the method?

If you do not use the Annealing method:

9. Why not?
10. How then do you treat unstable archaeological iron?

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Calls for collaboration

<u>Analysis of ancient artefacts made of glass, enamel and metal</u> (***RD/SHM***)

With this abstract, I am taking the opportunity to make contact with researchers working in the domains of materials analysis, old technologies, and corrosion processes and deterioration of ancient artefacts made of glass, enamel and metal.

Since I am engaged in the restoration of metal and enamel objects, I am currently involved in research related to old technologies of enamelling and new materials and methods for the conservation and restoration of enamel clock dials and jewellery.

The general theme is to compare the corrosion mechanisms of glass and metals. As a result of my observations of many years and experimental work, I came to a conclusion that the structure of glasses and metals could be regarded as two counterparts (opposite) models of structures of solid state. Accordingly to this concept, the investigations of corrosion processes in metals and glasses can be complementary.

The above mentioned, deep theoretical and practical researches of the interrelations of structure and corrosion processes of materials are necessary for the more detailed understanding of deterioration processes in glass and metal artefacts. In turn, this idea could help us to obtain more scientifically founded solutions to our problems in conservation and restoration of glass, metal and especially enamelled artefacts.

I have gathered and prepared a collection of metal and glass samples for such investigations.

A group of scientists equipped with SEM-EDS system helped me in this work. And we would be glad to join, to support or organize a special programme using this equipment for the material analysis needed to attribute and study old technologies in metal, glass, enamel work.

I would sincerely appreciate receiving your opinion on the general opportunities to continue working in this direction and the means of financial support for our investigations.

Contact: Marina Kozlova (RD/SHM)

General information

Future seminars and conference

- **Metallic Alloys, Research and Conservation** (13-14 November 2003, Porto, Portugal). Organised by the Conservation and Restoration Laboratory of the Heritage Sciences and Techniques Department of the University of Porto. For more information contact Paula Menino Homem (pmeninoh@clix.pt)
- **Benefits of Non-Destructive Analytical Techniques to the Knowledge of Museum Objects** (08-10 January 2004, Bighi, Kalkara, Malta). Seminar organised by COST Action G8, the Malta Centre for Restoration and the Institute of Masonry and Construction Research (University of Malta). For more information contact Christian Degrigny (cdegrigny@mcr.edu.mt) and consult http://srs.dl.ac.uk/arch/cost-g8
- **"Structuring Working Group 3 (Degradation process, corrosion and weathering)"** (13-14 February 2004, Wertheim-Bronnbach, Germany). Seminar organised by COST Action G8 and the Fraunhofer-Institut für Silicatforschung. For more information contact Christian Degrigny (cdegrigny@mcr.edu.mt)
- **Philosophy, ethics, history and mechanics of cleaning**, 2004 American Institute for Conservation (AIC) annual meeting (09-14 June 2004, Portland, Oregon). Session organised by the Object Speciality Group within AIC. For more information contact Alice Paterakis (alicepaterakis@yahoo.com)
- **Workshop on "Heritage Conservation/Corrosion of Archaeological Objects"** (*14 September 2004* -Nice (France) within the EUROCORR 2004 congress (12-16 September 2004). Organised by Philippe Dillmann, CEA & Gérard Béranger, UTC. Papers presented at this workshop will be published in the Proceedings of EUROCORR 2004 (CD-ROM). Abstracts should be submitted electronically to CEFRACOR via: www.scifrance.org/congres/eurocorr2004. Submission deadline January 16, 2004.

Abbreviations and acronyms

ANDRA: Agence pour la Valorisation des Déchets Radioactifs
CEA: Centre d'Etudes Atomiques
CNR-ISMN: Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati
COST: European Cooperation in the field of Scientific and Technical Research
CNRS: Centre National de Recherche
C2RMF: Centre de Recherche et de Restauration des Musées de France
DC/OCM: Department of Conservation, Odense City Museums
DMCUoM: Darling Marine Center, University of Maine
DSC: Danish School of Conservation
DCUoM: Department of Chemistry, University of Maine
EC or EU: European Commission or European Union
EDS: Energy Dispersive Spectroscopy
HA / RAFA: Hogeschool Antwerpen / Royal Academy of Fine Arts
HTACL: Head Tide Archaeological Conservation Laboratory
ICMCB : Institut de Chimie de la Matière Condensée de Bordeaux
ICN: Instituut Collectie Nederland
ICR: Istituto Centrale per la Restauro
IRAMAT: Institut de Recherche sur les Archéomatériaux
IRRAP : Institut de Restauration & de Recherches Archéologiques et Paléométallurgiques

ISC: Fraunhofer Institute for Silicate Research
LADIR: Laboratoire de Dynamique Interaction et Réactivité
LRC: Laboratoire de Recherche Correspondant
LRMH: Laboratoire de Recherche des Monuments Historiques
MCR: Malta Centre for Restoration
NIPM: National Institute for the Preservation of Monuments
RD/SHM: Restoration Department / State Hermitage Museum
RM: Rijksmuseum
SEM: Scanning Electron Microscope
UPR 15: Unité Propre de Recherche "Physique des Liquides et Electrochimie" of CNRS, University of Paris VI
UTC: Université Technologique de Compiègne
VB/GACC : Vologda Branch-office of the Grabar Art Conservation Centre
XRD: X-ray Diffraction
XRF: X-ray Fluorescence

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